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A highly crystallized glass candidate armor material known as SITALL has been prepared in plate form suitable for ballistic test and evaluation in complex composite armor systems designed to defeat chemical and kinetic energy threats. Two comparative test formulations of SITALLs were synthesized and characterized as to pertinent chemical and physical properties. The significance of this work is that it indicates the need to further develop crystallized glass formulations which result in crystallized glass formulations which result in crystalline phases which exhibit improved hardness values over those already achieved in these systems.

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Introduction

Crystallized glass-ceramics and its technology have been of interest to ceramic scientists and engineers for most of this century as a potentially useful material for a multitude of diverse applications. Glass-ceramics are in current use as pyroceram tableware and as automobile engine exhaust catalyst supports. Opal glasses and recrystallized lithium aluminosilicate glass systems are well known articles of commerce. Pyroceram cookware, missile radomes, and other miscellaneous items have a proven independent utility. The relatively low cost (less than one dollar per pound), as well as the ease of forming to simple and complex shapes through the use of conventional glass forming techniques, high strength, and low density (less than 2.5 g/cc) make this class of materials highly attractive for potential applications in armor systems designed to defeat chemical and kinetic energy munitions.

It is known that the conventional soda-lime-silica glasses possess a certain dilatation effect when subjected to shaped charge metal jet penetration. This perturbation effect apparently causes the shaped charge metal jet stream to become discontinuous, thereby rapidly losing velocity and direction resulting in its defeat.

It has long been desired to improve the effectiveness of glass-based compositions against shaped charge and kinetic energy projectiles through either increasing the hardness and/or elastic modulus of glass or through the incorporation of favorable crystalline phase materials. In addition, there are other requirements for such an improved armor material component including cost, low density, dimensional stability, and a prolonged resistance to chemical agents such as acids, bases, and water. The correlation of ballistic resistance with mechanical properties has not been available for such glass-ceramic systems.

Accordingly, it was thought desirable to secure and test a material known as SITALL which had been invented in the former Soviet Union and patented in the United States of America in 1984 as U.S. Patent Number 4.473,653 because reports of its use in the former Soviet Union as well as the U.S. Army Foreign Science and Technology Center information reports had referred to this SITALL group of materials as highly effective ballistic-resistant materials.

This material, SITALL, is known in the scientific community but has not been further researched, developed, or manufactured in the United States of America, nor is SITALL available on a reasonable or timely basis from foreign sources. It was decided to seek out a domestic source for this material with the assistance of the patent holder and which would afford the opportunity to rearrange the original formulation to obtain different combinations of glass/crystals and porosity in the test specimen products, as well as prove out the ability to make SITALL in the engineering shapes required. Due to the relatively small amount of material (less than 1,000 pounds) required for test and evaluation, none of the large well known glass and glass-ceramic manufacturers were willing to undertake supplying this material according to the required specifications. Through the intermediary efforts of Baker Associates, Inc. of Columbus, Ohio, the Jeannette Specialty Glass Company agreed to furnish the specified SITALL material in 6" x 6" x 1" thick plates and 12" x 12" x 1" thick plates as a subcontractor to Baker Associates, Inc; these are the items referred to in the subsequent text.

SITALL Glass-Ceramics

The SITALL glass-ceramics are essentially crystallized glasses and are known variously as "devitrified glasses," "devitrified ceramics," "vitro-ceramic" (Europe), and SITALLs (Russia). The term "pyroceram" is a glass-ceramic produced by Corning, Inc. and is a trademark name for this class of materials. Glass-ceramics are particular glass compositions which have been subjected to a carefully controlled devitrification or crystallization treatment. Glass-ceramic articles can be formed by conventional glass working techniques in forming through cooling from the molten viscous state. Subsequent processing results in a solid structure consisting of crystal particles in a usually unspecified amount of a matrix glassy phase.

The manufacture of glass-ceramics begins with the production of a glass of a sufficiently specialized composition that can be devitrified or crystallized by a suitable thermal treatment processing schedule after forming into an article. In general, special nucleating agents; e.g., TiO_2 which is an appropriate metal cation oxide, a fluoride, or an oxide; e.g., TiO_2, P_2O_5, or rare earth oxides are included in the composition to assist in devitrification.

After forming, this still-vitreous material is subjected to a thermal treatment process which results in the formation and growth of crystalline inclusions in the glass. In most cases, the heat treatment is performed in two steps:

- Heating produces crystalline nuclei (molecular clusters)
- Thermal treatment causes the crystals to grow upon the nuclei so formed to the desired size range

The heat treatment conditions, especially the rate of temperature increase and time duration at a particular temperature, strongly influence the ultimate crystal type and size, thereby having a profound influence upon the final material properties through influencing such factors as crystal type, relative amounts of crystalline phases precipitated, the crystal/glass ratio, and the crystal size. The procedure for forming the SITALL glass-ceramic plates was as follows.

The raw materials in the form of oxides and carbonates were batched from free-flowing powders through calculating the ratios of the specific compounds available commercially for yielding the final oxide content desired in the final product. The catalyst/nucleating agents; e.g., titanium oxide, zirconium oxide, and tin oxide in the ratio of 3:2:1 were batched from chemically pure reagent grade powders. The necessity for maintaining this particular ratio is carefully delineated in the instant patent with great emphasis. A 3,000 pound batch was weighed, mixed, and placed into a 6,000 pound glass-melting refractory pot and brought to the 1550°C melting temperature with gas heat. After a holding period of one hour accompanied by mixing, gobs of the glass were removed by collecting the molten gob on a steel rod and, using scissors, cutting off the gob, dropping it into a cast iron mold and hand pressing the gob into plate form with an upper platen plate. After forming, the plates were placed into an annealing oven and held at 480°C for four hours. The required complex multistep procedure for crystallizing the plates was performed in a 36-cubic-foot furnace. The exact crystallization procedure is shown in Figure 1.

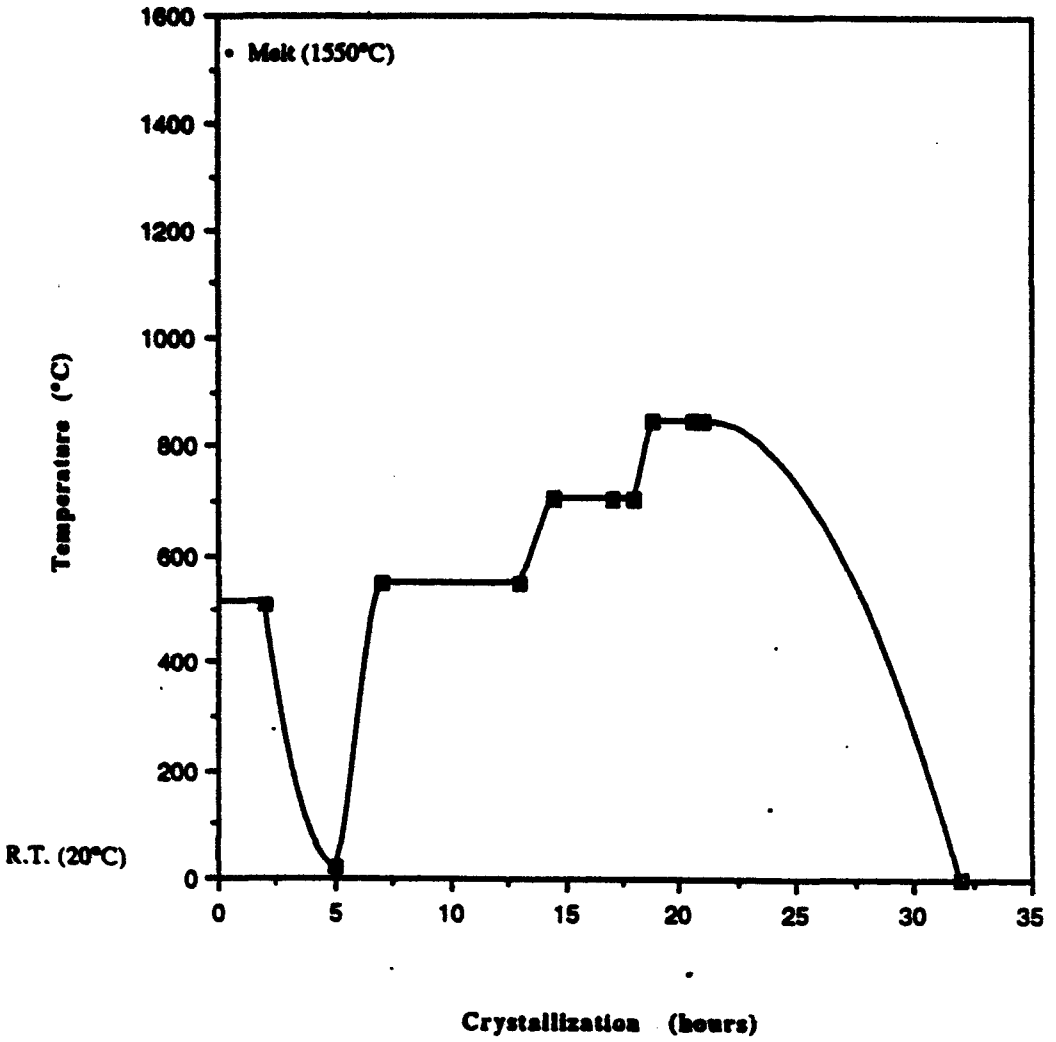

Figure 1. Preferred crystallization procedure for SITALL.

The plates as-formed in the cast iron molds were highly transparent but after the complex crystallization procedure the plates were opaque, similar to conventional opal glass. The square plates are 12" x 12" x 1" thick and 6" x 6" x 1" thick and appear to be a sound physical product suitable for ballistic test and evaluation.

SITALL Chemistry

The chemical composition of the SITALLs produced in plate form was found to be highly consistent and representative of the original raw batch formulation. In fact, the close agreement of these chemistries is noteworthy. It should be noted that the total of ingredients and chemical constituents does not always correspond to 100 percent because of the nature of the calculation of the quantitative chemical analyses (see Tables 1 and 2).

Table 1. Chemistry of SITALL batch compositions

Oxide	SITALL I (Weight %)	SITALL II (Weight %)
SiO_2	79.78	79.61
Li_2O	12.15	12.13
Al_2O_2	3.89	3.89
MgO	1.87	1.86
K_2O	2.04	2.03
Cr_2O_2	0.03	0.03
CeO_2	0.06	0.06
TiC_2	0.09	0.18
ZrO_2	0.06	0.12
SnO_2	0.03	0.06
B_2O_2		0.04
Total (%)	100.00	100.00

Table 2. Chemistry of SITALL plate compositions and glass

	SITALL I (Weight %)	SITALL II (Weight %)	Glass (Weight %)
SiO_2	76.2	76.2	72.3
Li_2O	15.6	15.6	
Na_2O			13.7
K2O	1.94	1.89	
CaO			10.4
MgO	2.09	2.06	2.6
CeO_2	0.18	0.19	
TiO_2	0.155	0.140	
ZrO_2			
SnO_2			
Al_2O_3	3.90	3.91	1.1
Cr_2O_3	0.027	0.022	
B_2O_3	<0.005	<0.005	
Total	100.097	100.037	100.1

SITALL - X-ray Diffraction Analysis

The two SITALL compositions were subjected to X-ray diffraction analysis to attempt to determine the type and amounts of specific crystalline and glassy constituents. The predominant crystal type found was dilithium silicate with very small amounts of a residual glassy phase (see Table 3).

Table 3. X-ray diffraction analysis of SITALLs

	Dilithium Silicate %	Amorphous %
SITALL I	95	5
SITALL II	95	5

NOTE: The SITALLs were apparently very highly crystallized.

Microstructure of SITALL I and SITALL II

The microstructure of these SITALLs was examined through conventional ceramographic sample mounting in acrylic resin blocks and abrasive polishing to secure optically flat surfaces for microscopic inspection. The resultant samples exhibited minor amounts of porosity (two to three percent) and a relatively large crystal size distribution. The SITALLs contained large amounts of grains in the one millimeter size range.

The SITALLs were also subjected to scanning electron microscope scrutiny and again were found to possess large amounts of irregular crystals in the size range of one to two millimeters in dimension, as well as very minor amounts of residual porosity.

Hardness of SITALL I and SITALL II

The SITALL compositions were tested for microhardness on a specialized Leitz pyramidal diamond point indent apparatus at the $Knoop_{100}$ gram weight level. The results are shown in Table 4.

The comparative data for similar glass-ceramic materials is also shown for reference. Please note the slightly softer nature of the SITALL compositions.

Table 4. Microhardness of SITALL I and SITALL II ($Knoop_{100}$)

Material Identification	Microhardness
SITALL I	530
SITALL II	550
Corning Pyroceram (Li_2O-Al_2O_3-SiO_2)	690
Glass (Soda-Lime-Silica)	600
CER-VIT	620
European Glass-Ceramic	600-650

Non-Destructive Evaluation of SITALLs

The SITALLs were subjected to an ultrasonic C-scan multipulse scanning technique. The results indicated a well crystallized microstructure which exhibited a small amount of very uniformly distributed porosity.

In Figure 2, the uncrystallized base glass exhibits the uniformity to be expected of a material formed through the usual batch melting and press forming to shape technique with very little porosity. Note the tiny yellow areas.

In Figure 3, the SITALL crystallized glass demonstrates excellent uniformity in the basic crystalline structural matrix with the very small amount of residual porosity shown as yellow spots very evenly distributed.

The conclusion to be drawn from the nondestructive testing is that the SITALL products were very well melted and formed to shape and crystallized in a very highly uniform fashion.

Summary and Conclusions

An experimental/developmental project to prepare two crystallized glass SITALL compositions in plate form suitable for incorporation into armor systems for ballistic test and analysis was successfully accomplished.

This project demonstrated that it is apparent that may SITALL compositions could be prepared in plate form for suitable experimental/developmental purposes.

The primary crystal phase of these SITALLs is DILITHIUM SILICATE with only very small amounts of residual porosity remaining due to the volume contraction from glass to crystal form.

These SITALLs have been reasonably well characterized providing a baseline for potential further study upon the development of these materials.

Ballistic test results are available and will be presented as an Addendum under separate cover. The support to TACOM through funding this project is gratefully acknowledged.

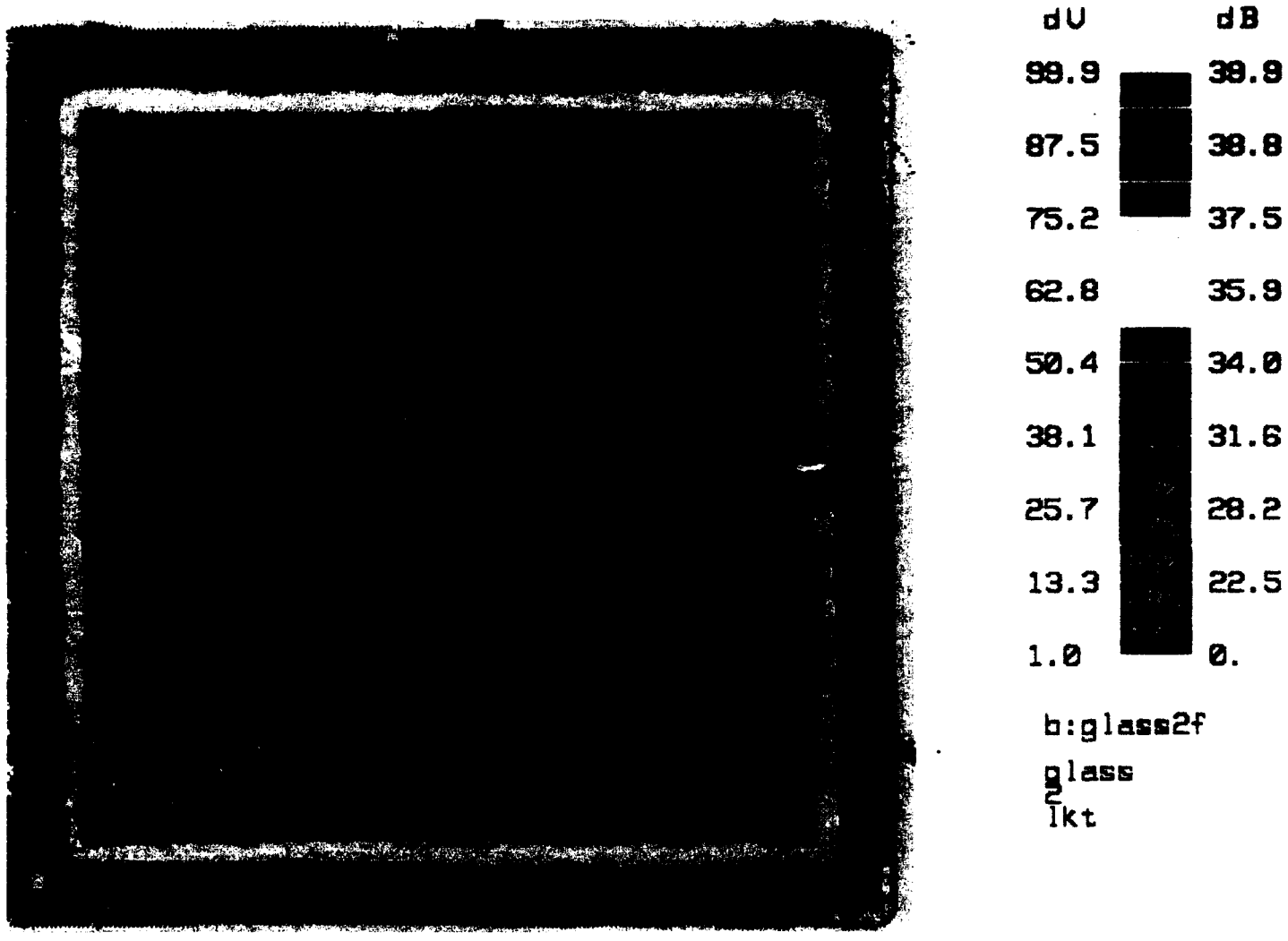

Figure 2. Base Glass, Uncrystallized.

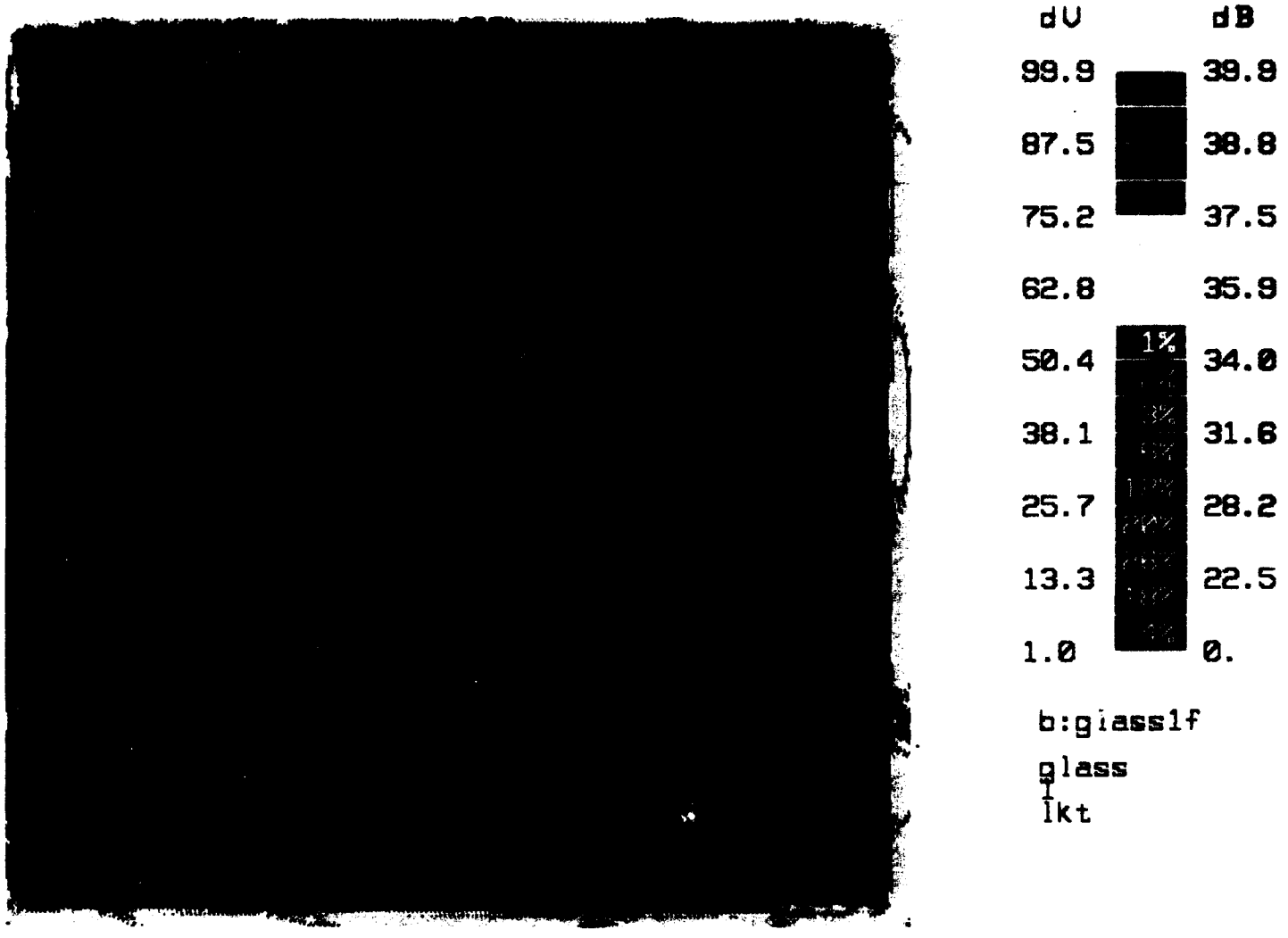

Figure 3. SITALL, Crystallized Glass.

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